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Hydrothermal method for the production of reduced graphene oxide



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HIGHLIGHTS

- We fabricate reduced graphene oxide (RGO) with a hydrothermal method.
- Higher reaction temperature can accelerate the reduction of GO more thoroughly.
- Poor conductive properties of RGO is that it may have some functional groups.
- The mechanism in the reaction process is discussed.

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ABSTRACT

Reduced graphene oxide, RGO (also called chemically modified graphene, CMG) was synthesized by a simple hydrothermal method, with graphite oxide (GO), prepared by the modified Hummers method, served as the raw material. Structural and morphological studies indicate the degree of reduction is dependent on the temperature, which is also verified by Raman analysis. The variation in interlayer distance and the intensity ratio of the D to G Raman modes (I_D/I_G) indicates higher reaction temperature can accelerate the reduction of GO. The conductivity also varies with the degree of reduction, as verified by electrochemical analyzer. Moreover, the reaction process affects organic functional groups, the mechanism during the reaction process is discussed.

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1. Introduction

Graphene, a single layer of sp^2 -bonded carbon atoms packed in a hexagonal lattice, since the first fabrication via a “Scotch tape” method in 2004 [1], has triggered great research interests. The fascinating properties of graphene, such as high thermal conductivity (5000 W/mK) [2], fast charge carrier mobility ($200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [2] and massless relativistic carriers [3], have been well described. Graphene and reduced graphene oxide, RGO (also called chemically modified graphene, CMG), are promising candidates as components in applications, such as energy-storage materials [4], catalyst supports [5] and electronic devices [6].

Graphene is usually prepared by Scotch tape method [1], chemical vapor deposition (CVD) [7–9] and epitaxial growth [10,11], which can yield graphene with a relatively small number of defects. However, these surface-based techniques do not scale well for applications requiring macroscopic quantities of graphene. For CVD, it is commonly required high reaction temperature, which

restricts the reaction to a certain extent. Exploring simple method to synthesize large-scale graphene is necessary. Solvothermal reaction is an alternative [12], which enables high yield of the products at low reaction temperature. Solvothermal process is known for the simple operation, mild synthesis conditions, and capability of deliver relatively large quantities. Several processes have been developed previously for nanostructured carbon materials. For example, diamond was synthesized via the reaction of tetrachloromethane and sodium [13] and carbon nanotubes (CNTs) from the reaction of hexachlorobenzene with metallic potassium catalyzed by Co/Ni [14]. Although solvothermal reaction can produce graphene, the product contains significant numbers of oxygen-containing functional groups and irreversible lattice defects. On the other hand, it usually generates graphene-like film exhibiting a relatively low C:O ratio and a considerable amount of residual functional groups, resulting in a highly resistive film [15,16]. In this study, we fabricated reduced graphene oxide (RGO) from the reduction of graphite oxide (GO) by solvothermal method at different temperatures, by systematically analyzing the influence of reaction temperature on the interlayer distance and the intensity ratio (I_D/I_G) of the D to G Raman modes of the as-produced RGO, we find that the degree of reduction is related with the reaction temperature, the conductivity in turn related with the

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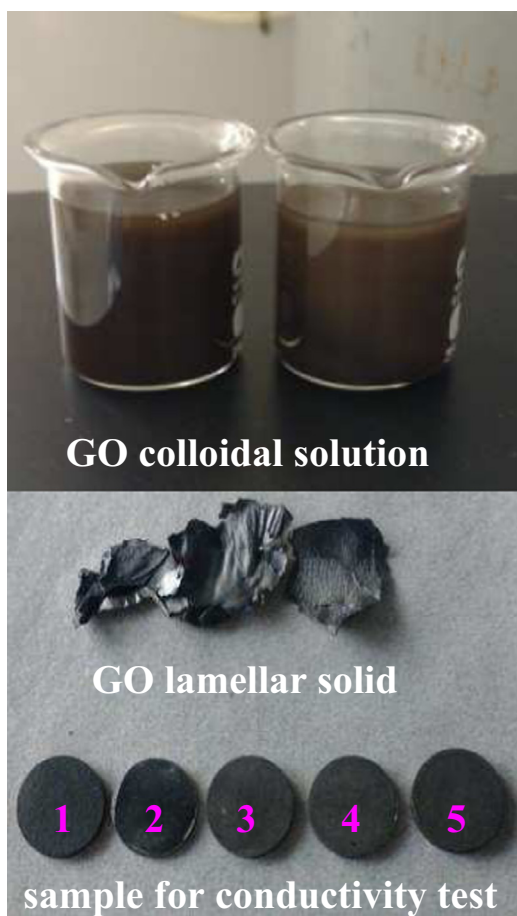


Fig. 1. The macroscopic physical samples.

degree of reduction. In addition, we speculate that the reaction mechanism is: graphite $\xrightarrow{\text{Oxidation}}$ GO $\xrightarrow{\text{Reduction}}$ RGO, and use it to successfully explain the reason why the change of layer spacing and oxygen content happens.

2. Experimental details

2.1. Synthesis of GO

Graphite oxide was prepared from natural graphite by the well-known Hummers method [17]. In a typical synthesis process, 1 g graphite powder was added to 23 ml concentrated H_2SO_4 at 0 °C, then 3 g KMnO_4 was added gradually under magnetic stirring under the temperature of 15 °C. The mixture was then stirred at 35 °C for another 40 min, followed by slowly increasing the temperature to 98 °C. Simultaneously, 46 ml of distilled water was slowly added and the mixture was maintained at that temperature for 20 min under reflux condition. At the end of the reaction, 140 ml of distilled water followed by 10 ml of 30% H_2O_2 solution was added. At this point, a golden solution was formed. The solid product was separated by centrifugation, washed repeatedly with 5% HCl solution until SO_4^{2-} could not be detected with BaCl_2 , then washed several times with acetone and water. In the end, the sample was dried in a vacuum oven at 60 °C overnight. Some lamellar solids were finally obtained for further experiments.

2.2. Prepare RGO by solvothermal reduction

First, 50 mg as-synthesized GO was suspended in 25 ml ethylene glycol to give a brown colloidal solution by 30 min of sonication. After that, the solution was sealed in a 50 mL Teflon-lined autoclave and maintained at different temperatures for 16 h. Then the solids were filtered and washed with acetone and distilled water several times. Finally, the collected sample was dried in a vacuum oven at 65 °C overnight. To simplify, we name the samples obtained at the temperatures of 140 °C, 160 °C, 180 °C as sample $\text{RGO}_{140\text{ °C}}$, $\text{RGO}_{160\text{ °C}}$, $\text{RGO}_{180\text{ °C}}$, respectively.

2.3. Characterization

Structural and morphological studies were done by means of X-ray diffraction (XRD) technique using $\text{Cu K}\alpha$ irradiation on an 800 W Philips 1830 powder diffractometer and Field-emission scanning electron microscopy (FESEM) measurements were acquired using a Hitachi S-4800 microscope instrument and accelerating voltage of 15 kV. The Raman spectra were measured using a micro-Raman spectrometer with 633 nm laser as excitation source. Transmission electron microscopy (TEM) images were recorded on a Hitachi H-7650 Transmission Electron Microscope operated at 110 kV. Electronic properties were measured with cyclic voltage method using the electrochemical workstation of CHI660B model with Init E (V) of -10 to $+10$, Sample Interval (V) of 1e^{-6} – 0.064 , Sensitivity (A/V) of 1e^{-12} – 0.1 . All the measurements were performed at room temperature under the same conditions. The macroscopic physical samples are shown in Fig. 1

3. Results and discussion

Fig. 2a shows the XRD patterns of RGO, to verify the degree of reduction, we also give the XRD patterns of intrinsic graphite and GO for comparison. The interlayer distance obtained from the (002) diffraction peak was 3.4 Å in graphite. After oxidation, great changes take place, strong (001) diffraction peak corresponding to GO appears combined with the disappearance of (002) diffractive peak, the (001) diffractive peak of GO located at 11.5° is equivalent to interlayer distance of 7.72 Å, which is much larger than that of pristine graphite. The large interlayer distance is attributed to the formation of hydroxyl, epoxy, and carboxyl groups [18].

Compared to the parent GO, after hydrothermal reaction, the (002) diffraction peak of graphite appears at about $2\theta=23^\circ$ combined with the disappearance of (001) diffraction peak of GO for all reduced samples prepared at different temperatures; however the (002) diffractive peaks are very wide compared to that of pristine graphite. But at 140 °C, there is another peak at around $2\theta=15^\circ$, which is generally considered as the peak of graphene oxide. The interlayer distance d_{002} decreases obviously but is still higher than that of well-ordered graphite, 3.4 Å (see Fig. 2b). The slightly larger interlayer distance may be due to the presence of residual oxygen and hydrogen, indicating incomplete reduction of GO sheets [19]. More significant is that the higher the temperature, the smaller the d_{002} , which indicates a higher temperature can restore GO more thoroughly. The weak and broad (002) diffraction peak is probably the results of disorderly stack of the graphite atoms along the c -axis direction. Another possibility is that the samples contain some scattered pieces of graphene sheets [19].

Raman spectroscopy is a very useful method to characterize the degree of reduction of GO. For all carbonaceous materials, both D and G bands are the predominant features in the Raman spectra; they are represented by peaks at around 1324 – 1346 cm^{-1} , 1490 – 1691 cm^{-1} , respectively [20]. Pristine graphite, as expected, displays a prominent G peak as the only feature at 1584.5 cm^{-1} ,

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